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A porosity-based corrosion model for alkali halide ash deposits during biomass co-firing

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Abstract

This paper presents a physics-based model to describe accelerated corrosion due to alkali halide-containing deposits, which form on superheater tube walls during biomass co-firing. Increased rates of corrosion during the co-firing of peat with biomass have been identified as a limiting factor on the level of biomass which is viable to use at elevated temperatures. In the present work a synthetic salt, representative of a 70:30 peat-biomass mix, has been applied to pure iron samples in air at 540 °C and 600 °C. The corrosion layers have been examined using scanning electron microscopy (SEM), optical microscopy and energy dispersive X-ray (EDX) spectroscopy elemental mapping to provide insight into the material degradation and structure of the corrosion layer. Two distinct types of oxide are found to form on the iron substrate. Initially, a compact, uniform oxide layer forms over the substrate. As the process continues, this oxide layer degrades, leading to spalling which sees the broken oxide pieces mix with the salt layer. Additional test samples were examined without deposits as controls to highlight the accelerated rate of corrosion. Two modelling techniques are examined; the widely-used labyrinth factor method (LFM) and the newly proposed porosity-based corrosion method (PCM). The PCM method uses measurements of porosity and pore radius, coupled with a physically-based corrosion mechanism, to predict corrosion rates. Results from the two modelling techniques are compared and both agree satisfactorily with experimental measurements for times of up to 28 days.

Keywords: biomass, co-firing, corrosion, fluidized bed, oxidation, power generation, high temperature, SEM, modelling, iron


**Introduction**

Due to worldwide demand for inexpensive, efficient electricity, which meets increasingly stringent environmental standards, there is a need to increase production of energy from renewable sources. Operators of thermal power plants are now investigating co-firing biomass, with fossil fuels. The addition of biomass results in an altered ash composition, which can result in elevated levels of corrosion, slagging and fouling\(^1\text{-}^5\). It has been found that co-firing biomass leads to an increased rate of corrosion of the superheater tubes in the plant. This increased corrosion rate occurs as a result of a combination of exposure to the flue gas, which contains Cl\(_2\) and HCl, and corrosion following deposition of alkali halides on superheater tubes. The accelerated corrosion due to both gaseous and deposit-based attack follow a chemical process known as active oxidation\(^6\). It has been found that the most severe corrosion problems in biomass fired boilers are associated with deposits containing alkali chlorides on the superheater tubes of the boiler\(^6\text{,}^7\). An example of the deposits on superheater tube walls in-situ at a fluidized bed power plant in Ireland, and the corroded pipes following removal from the plant is shown in Figure 1, which has been provided by ESB.

![Figure 1: An example of in-situ deposits on superheater tubes and tubes showing heavy corrosion following removal (Courtesy of ESB)](image)

Work carried out by Abels et al.\(^8\) has shown that Cl\(_2\), and not HCl, is the main aggressive species in this corrosion process, at least for short exposure times; hence the initial reactions in this study are based
on Cl₂. Figure 2 shows the active oxidation process as it proceeds for superheater tubes in-situ. In this mechanism alkali halide salts, which are typically in the form of alkali chlorides (MCl), are released during the combustion process, travel in the flue gas and deposit on the tube walls. On the tube walls, the mixed salts form a eutectic melt, whose melting temperature is lower than any single salt. Chlorine is released from the halide melt via chemical reaction with the outer oxide layer of the metal (Fe₂O₃) (R1). One of the products of this reaction is free chlorine (Cl₂), which migrates to the oxide/metal interface and reacts with the uncorroded metal surface to form iron chloride initially as a solid (FeCl₂ (s)) (R2). The focus of the current study is to develop a physics-based model for accelerated corrosion and validate it for pure iron, hence Cl₂ is assumed to react solely with Fe. The iron chloride then evaporates to form iron chloride gas (FeCl₂ (g)) due to the high volatility of the chloride (R3). In alloyed metals the chlorine will react with other elements and form additional chlorides.

As the metal chloride gas has a high vapor pressure, as shown in Figure 3, it then diffuses outward to the oxide surface, where it reaches higher levels of oxygen concentration. Once oxygen partial pressure is increased sufficiently iron chloride is oxidized to iron oxide (Fe₂O₃) (R4). As the conversion of the metal chlorides to oxides (R4) occurs, cracks and pores grow in the oxide scale, leading to subsequent cracking and spalling, which results in a non-protective, loosely adherent oxide scale being formed. The released chlorine is also now free to restart the cycle or is itself converted to HCl in the high moisture flue gas (R5).

\[
\begin{align*}
2\text{MCl} + \text{Fe}_2\text{O}_3 + \frac{1}{2} \text{O}_2 & \rightarrow \text{M}_2\text{Fe}_2\text{O}_4 + \text{Cl}_2 & \text{M} = \text{K}, \text{Na} & \text{R1} \\
\text{Cl}_2 + \text{Fe} & \rightarrow \text{FeCl}_2 (s) & \text{R2} \\
\text{FeCl}_2 (s) & \rightarrow \text{FeCl}_2 (g) & \text{R3} \\
2\text{FeCl}_2 + \frac{3}{2} \text{O}_2 & \rightarrow \text{Fe}_2\text{O}_3 + 2\text{Cl}_2 & \text{R4} \\
\text{Cl}_2 + \text{H}_2\text{O} & \rightarrow 2\text{HCl} + \frac{1}{2} \text{O}_2 & \text{R5}
\end{align*}
\]
Figure 2: Schematic of tube wall corrosion via active oxidation

It has also been suggested that SO$_2$ in the flue gas can initiate the active oxidation process via reaction R6. The active oxidation process can then proceed via reactions R2, R3 and R4 as previously stated.

$$2\text{MCl} + \text{Fe}_2\text{O}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{M}_2\text{Fe}_2\text{O}_4 + \text{Cl}_2 \quad \text{(R1)}$$

$$\text{Cl}_2 + \text{Fe}/\text{Ni}/\text{Cr} \rightarrow \text{FeCl}_2 \quad \text{(R2,3)}$$

$$2\text{FeCl}_2 + \frac{3}{2} \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 2\text{Cl}_2 \quad \text{(R4)}$$

The presence of SO$_2$ in the environment has been shown to have positive or negative effects on corrosion rate. It has been found that the corrosion process can be severe in air but can also be increased modestly by the presence of SO$_2$ which can cause intra-deposit sulfation of alkali chlorides releasing HCl or Cl$_2$ close to the metal surface$^{6,10,11}$. Lith et al.$^{12}$ showed that the degree of sulfation of KCl in the deposit in the presence of SO$_2$ does not necessarily influence corrosion rate. An increase in SO$_2$ has also been shown to decrease corrosion rate through conversion of KCl in the flue gas to the less corrosive K$_2$SO$_4$$^{13,14}$. The presence of HCl in the flue gas results in an enhanced corrosion rate as sulfates in the deposits are converted into mixed chlorides which react with the oxide scale and form free chlorine. A combination of HCl and SO$_2$ in flue gas is found to be less harmful, as the sulfates found in the deposits are stabilized and less reactive$^{10}$ in the presence of SO$_2$. 
In addition to the complexities due to the environmental conditions alloyed steels also present complications. The chlorine that travels through the oxide and forms iron chloride can also react with other components of the alloy to form chlorides such as chromium chloride (CrCl\textsubscript{2}). Potassium and sodium in the salt are also known to participate in corrosion of stainless steels, leading to formation of alkali chromates\textsuperscript{15} which destroy the protective chromium oxide scale on stainless steels. This allows the released chlorine to penetrate through the oxide and reaction R2 can occur between the chlorine and metal at the metal/oxide interface\textsuperscript{16,17}.

The path of active oxidation for alloyed steels follows the same reactions as shown, with the different elements in the alloy reacting in the place of iron with the chlorine at different pressures. The vapor pressures of iron and chromium chloride and their temperature dependencies are shown in Figure 3. Figure 3 also shows that iron chloride can be expected to diffuse outwards at a greater rate than chromium chloride due to its higher vapor pressure. It is important to note that the values presented are for pure metal chlorides; in the case of alloys, mixed chlorides will form and their vapor pressures can only be estimated from those presented here\textsuperscript{18}. As chromium chlorides are less volatile than iron chlorides, they are oxidised closer to the metal surface\textsuperscript{19}. Iron chloride needs significantly higher oxygen pressure to convert to iron oxide and thus has to travel further out through the oxide to reach higher oxygen partial pressures, leading to detachment from the substrate.
It has been shown that the rate controlling step of the active oxidation process is the outward gas diffusion of the FeCl$_2$ gas through the cracks and pores in the oxide layer to the higher concentrations of oxygen$^{10}$. The thermodynamic stability of metal chlorides and oxides at a given temperature depends on the partial pressures of oxygen and chlorine$^{18}$. The thermodynamic phase stability diagram for the Fe-O-Cl system at 540 °C can be calculated using chemical reaction and equilibrium software and is shown in Figure 4.
Previous work has included the development of custom experimental rigs\textsuperscript{20} which attempt to replicate fluidized bed combustors as well tests in which samples are exposed to gas flows containing HCl or similar gases\textsuperscript{21,22}. Work has also been conducted in which corrosion probes were placed in a biomass CHP plant\textsuperscript{23}. A review of recent research on ash-related issues in fluidized bed combustion of biomass has been carried out by Hupa\textsuperscript{1} while a review paper focusing specifically on the chlorine-associated corrosion in biomass boilers was carried out by Nielsen et al.\textsuperscript{6}.

The present work represents the initial steps to develop and validate a physics-based model to model the corrosion process that occurs during the co-firing of peat and biomass mixtures in fluidised bed combustion systems. Fluidised bed units are the focus of research in this field due to their relatively high degree of flexibility of fuel type and particle size. This model is envisioned to be used as a pre-screening method to predict the corrosion depth on superheater tube materials for long term, high temperature tests and help reduce the number of tests required. It is not expected to eliminate the need for long-term experimental and in-situ testing. Experiments are carried out to gain greater understanding.

*Figure 4 Phase stability diagram of Fe-O-Cl system at 540 °C*
of the corrosion process and for use in calibration and validation of existing and proposed models. The models focus on the corrosion occurring as a result of the chlorine-containing deposits on the tube walls which are currently considered to be the most significant agents of corrosion. A number of models have been developed in previous work to determine the growth of corrosion layers on metals\textsuperscript{10,11,24}.

The focus of the current work is on model validation. For this reason, experiments are performed in air, not flue gas, and using pure iron, not materials found in operational plants. Future work will investigate the effects of flue gas composition on the corrosion process and incorporate these effects into the model. Future work will also involve grade 91 steel and other alloys.

The next section of this paper will describe the experimental methodology and the basis behind it. The modelling section will discuss the two modelling methods used. Results obtained from the experiments and the modelling are then discussed and compared, leading to the conclusions.

**Experimental**

The experimental method used in the present work is similar to that of Skrifvars et al.\textsuperscript{26, 27} in which synthetic salts are deposited on metal specimens and placed in high temperature furnaces. A schematic of the method used here is shown in Figure 5.
Ash compositions have been obtained from in-situ tests carried out by industrial collaborators for various levels of co-firing. Following identification of the target composition a range of starting materials including NaCl, KCl, Na₂SO₄, K₂SO₄, NaBr, KBr, MgSO₄ and CaSO₄ were obtained. Using stoichiometry and mass and molar fractions, the quantities of the starting materials to be mixed to obtain a similar ash composition were identified. These were mechanically mixed together, melted at 1100 °C in an alumina crucible, quenched to room temperature and ground to a particle size of less than 250 μm.

The compositions of the plant ash deposition from a 70% peat, 30% woodchip mixture and the associated representative synthetic salt are shown in Table I by weight percentage.

Ash composition by molar percentage is 4.64% KCl, 3.31% Na₂SO₄, 2.49% K₂SO₄, 0.07% KBr, 9.94% MgSO₄, and 79.55% CaSO₄. Peat ash contains high concentrations of calcium, which is present as CaO, Ca(OH)₂ and calcium silicates. In the combustion furnace, CaO quickly reacts with SO₂/SO₃ to form CaSO₄. CaO is not present in the synthetic salt due to its short lifespan in the deposits. CaSO₄ decomposes at temperatures greater than 1000 °C, but remains stable at 540-600 °C. The maximum
temperature reached in the fluidised bed plants, relevant to this work is 920 °C, thus the amount of CaSO$_4$ in the fly ash remains high.

<table>
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<tr>
<th>Element wt. %</th>
<th>Na</th>
<th>K</th>
<th>Cl</th>
<th>Br</th>
<th>S</th>
<th>Mg</th>
<th>Ca</th>
<th>Si</th>
<th>Fe</th>
<th>Al</th>
<th>Ni</th>
<th>P</th>
<th>Cr</th>
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</thead>
<tbody>
<tr>
<td>Plant ash deposit</td>
<td>2.09</td>
<td>5.21</td>
<td>2.18</td>
<td>0.07</td>
<td>21.59</td>
<td>3.54</td>
<td>44.35</td>
<td>5.87</td>
<td>9.70</td>
<td>1.70</td>
<td>0.94</td>
<td>1.51</td>
<td>1.23</td>
</tr>
<tr>
<td>Synthetic salt</td>
<td>2.12</td>
<td>5.27</td>
<td>2.29</td>
<td>0.07</td>
<td>42.25</td>
<td>3.36</td>
<td>44.36</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Previous work has studied the effect of KCl, NaCl, K$_2$CO$_3$, as well as combinations of NaCl, Na$_2$SO$_4$ and K$_2$SO$_4$ on metals$^{15,25–27}$. However these studies do not include the influence of Ca. Due to the large percentage of calcium present, as determined from in-situ test data from industrial partners and previous work$^{23}$, it is considered important to investigate its impact on the corrosion process. It is noted that bromine is present in the synthetic salt and is expected to contribute qualitatively to the corrosion process in a manner similar to chlorine. However due to its relatively low content (0.07 wt. %) it is not considered to be significant here and is therefore not included in the model.

Metal specimens of pure iron (99.5% purity) were cut to size 10 mm $\times$ 10 mm $\times$ 3 mm and then ground on 240, 320, 400, 600 and 800 grit silicon carbide paper, cleaned and pre-oxidised at 200 °C for 24 hours, in order to produce an initial protective oxide layer on the samples. The synthetic salt was applied to 6 samples of iron and placed in a furnace at 540 °C. A further 6 samples of iron were also placed in the furnace with no salt coverage. Samples were removed from the furnace after 1, 4, 7, 14, 21 and 28 days. Three characterisation techniques were carried out on the sectioned samples; scanning electron microscopy (SEM), optical microscopy (OM) and energy dispersive X-ray spectroscopy (EDX).

The samples were removed from the furnace, fixed in epoxy and cut to reveal a cross sectional area of the sample. Figure 6 shows a sample following exposure for 7 days before being fixed in epoxy. The
arrow indicates the section which is analysed. This sectional plane was ground using 240, 320, 400, 600, 800 and 1200 grit SiC grinding paper and polished progressively using 30, 6 and 3 μm diamond paste. In order to preserve the integrity of the chlorides and other water-soluble compounds on the samples, post-test polishing was done without a lubricant\textsuperscript{11,12}.

![Sample following exposure at 540 °C for 1 week with salt coverage, with arrow indicating section to be analysed](image)

The samples were then examined using an Olympus BX51M optical microscope and a Hitachi S-4700 scanning electron microscope (SEM), to measure the depth of corrosion and provide insight into the subsurface material degradation and structure of the corrosion layer.

Energy dispersive X-ray spectroscopy (EDX) analysis was also carried out to provide information regarding the chemical composition at different depths. Elemental maps were created in order to obtain the complete chemical composition of a section of the sample. Corrosion depth distributions have been quantified using the microscopy techniques in a manner similar to Nielsen et al.\textsuperscript{11}, Frandsen\textsuperscript{2} and Dudziak et al.\textsuperscript{28}. The corrosion depth is defined as the sum of the thickness of the oxide layer and the degraded material\textsuperscript{25}. An average thickness was calculated from measurements taken at 15-20 different locations across the specimen width.
Modelling

This paper presents two models for the accelerated corrosion due to alkali halide-containing deposits and the active oxidation mechanism. These are (1) the previously used labyrinth factor method (LFM) and (2) the newly proposed porosity-based corrosion method (PCM). The models are compared with each other and with experimental results. A schematic of the corrosion process being modelled is shown in Figure 7. This image displays the salt layer resting on top of a porous oxide layer. Cl$_2$ is released and travels through the oxide until it reaches the iron. Once there, it reacts to form FeCl$_2$(s) which then diffuses outwards as FeCl$_2$(g). The model currently assumes a single, porous protective layer of oxide, which continues to grow with time as shown by the growth between (a) and (b). Oxide layer growth is due to (1) degradation of the iron substrate and (2) the lower density of Fe$_2$O$_3$ deposited in the oxide layer. This is a simplification of the plant process which will involve sections of multiple layers of oxides forming and breaking away from the substrate.

Assuming the rate controlling step of the corrosion process to be the outward diffusion of FeCl$_2$ gas through the porous oxide layer, Fick’s law as shown in Equation 1, forms the basis for the model of the
corrosion rate:

\[ J_A = -D_{\text{Eff, A}} \frac{dC_A}{dz} \]  

Equation 1

where \( J_A \) is the flux of species A, \( D_{\text{Eff, A}} \) is the effective diffusion coefficient of A through the porous oxide layer, \( C_A \) is the concentration of the gas A in the gaseous mix and \( z \) is the depth into the substrate. All chemical reactions are assumed to be in chemical equilibrium since they proceed rapidly compared to the diffusion of FeCl\(_2\). Therefore, chemical reaction kinetics are neglected. The concentration of gas A in the mixture is the driving force for the diffusion rate in this expression. This can be related to pressure via the ideal gas law which results in Equation 2.

\[ J_A = -\frac{D_{\text{Eff, A}}}{R_A T} \frac{dP_A}{dz} \]  

Equation 2

where \( R_A \) is the specific gas constant of the gas diffusing outward and \( T \) is the temperature. In the present work, gas A is identified as FeCl\(_2\). \( R_{\text{FeCl}_2} \) is the specific gas constant for FeCl\(_2\) and is calculated via Equation 3.

\[ R_{\text{FeCl}_2} = \frac{\mathcal{R}}{M_{\text{FeCl}_2}} \]  

Equation 3

where \( \mathcal{R} \) is the universal gas constant and \( M_{\text{FeCl}_2} \) is the molecular weight of FeCl\(_2\). FeCl\(_2\) partial pressure varies as it diffuses out through the oxide layer and reaches higher concentrations of O\(_2\). Once it reaches a sufficiently high concentration of O\(_2\), Reaction R4 occurs and the FeCl\(_2\) converts to Fe\(_2\)O\(_3\), with Cl\(_2\) being released to repeat the process. For this model, temperature-dependent partial pressures are obtained at the metal-oxide interface via calculation of the FeCl\(_2\) (g) vapor pressure from reaction R3. The partial pressure at the oxide scale surface has previously been found to be negligible\(^{10,24}\). Equation 4 is obtained by integrating Equation 2 through the oxide layer thickness \( (l_{\text{Ox}}) \) and assuming
all variables are uniform except \( P_A \), which has been identified as \( P_{FeCl_2} \).

\[
J_{FeCl_2} = \left( \frac{D_{Eff,FeCl_2}}{l_{Ox} R_{FeCl_2} T} \right) \left( p_{i,FeCl_2} - p_{s,FeCl_2} \right) \tag{Equation 4}
\]

where \( p_{FeCl_2} \) is the partial pressure of the FeCl\(_2\) gas with \((i)\) and \((s)\) designating the interface of substrate and oxide and the surface of the oxide respectively. This results in an expression similar to those obtained by Grabke et al.\(^{10}\) and Stott & Shih\(^{24}\). There will potentially be secondary gaseous components, e.g. O\(_2\) and Cl\(_2\), present in the system. These are not explicitly accounted for due to their secondary importance. The values of the variables and constants used in the calculations are shown in Table II. The constants identified from experimental data are detailed in the results section. Figure 8 shows the definitions of key variables used in the model in schematic form and on an SEM image.

\[ajo\]

**Figure 8** Definitions of key variables used in oxide depth calculations on (a) SEM image and (b) and idealised physical model

From mass conservation the following expression is obtained:

\[
\frac{dl_{Fe}}{dt} = \frac{J_{Fe}}{\rho_{Fe}} \tag{Equation 5}
\]

where \( l_{Fe} \) is the depth of the iron which is converted to iron oxide in the sample and \( \rho_{Fe} \) is the density of iron. Assuming that all Fe leaves the system as FeCl\(_2\), the rate of flux of iron can be related to the flux of iron chloride via the ratio of their respective molecular weights as shown in Equation 6.
\[ J_{Fe} = \frac{M_{Fe}}{M_{FeCl_2}} J_{FeCl_2} \]  \hspace{1cm} \text{Equation 6}

where \( M_{Fe} \) and \( M_{FeCl_2} \) are the molecular weights of Fe and FeCl\(_2\) respectively. From Equations 4 to 6, an expression is obtained for the depth of iron which is converted to oxide with respect to time and is shown in Equation 7.

\[ \frac{dl_{Fe}}{dt} = \frac{D_{Eff,FeCl_2} M_{Fe} \rho_{Fe} R_{FeCl_2} T_{Ox}}{M_{FeCl_2} \rho_{Fe} R_{FeCl_2} T_{Ox}} \]  \hspace{1cm} \text{Equation 7}

The depth of iron converted to oxide, \( l_{Fe} \) must now be related to the depth of oxide formed \( l_{Ox} \). In order to do this we assume that for every 2 moles of Fe removed from the substrate 1 mole of Fe\(_2\)O\(_3\) is deposited in the oxide layer, from reactions R2 and R4. The amount of moles of Fe are hence related to the number of moles of oxide via Equation 8.

\[ \frac{dN_{Fe}}{dt} = -2 \frac{dN_{Fe,O_3}}{dt} \]  \hspace{1cm} \text{Equation 8}

where \( N_{Fe} \) is the number of moles of iron consumed and \( N_{Fe,O_3} \) is the number of moles of oxide produced. This is then related to the mass of the iron consumed and oxide produced by via molecular weights and Equation 9 is obtained.

\[ \frac{1}{M_{Fe}} \frac{dm_{Fe}}{dt} = \frac{-2}{M_{Fe,O_3}} \frac{m_{Fe,O_3}}{dt} \]  \hspace{1cm} \text{Equation 9}

where \( m_{Fe} \) is the mass of the iron consumed, \( m_{Fe,O_3} \) is the mass of oxide produced and \( M_{Fe,O_3} \) is the molecular weight of Fe\(_2\)O\(_3\). By relating the volume and density of both the iron consumed and the oxide produced an expression linking the depth of iron with the depth of oxide is produced as shown in Equation 10.

\[ \frac{dl_{Fe}}{dt} = -2 \frac{M_{Fe}}{M_{Fe,O_3}} \frac{\rho_{Fe,O_3}}{\rho_{Fe}} \frac{dl_{Ox}}{dt} \]  \hspace{1cm} \text{Equation 10}
where \( \rho_{\text{Fe}_2\text{O}_3} \) is the density of \( \text{Fe}_2\text{O}_3 \). By combining Equation 10 with Equation 7 an expression for the growth of the oxide layer with time is obtained as shown in Equation 11.

\[
\frac{dl_{\text{Ox}}}{dt} = \frac{1}{2 \rho_{\text{Fe}_2\text{O}_3} M_{\text{FeCl}_2}} \frac{M_{\text{Fe}_2\text{O}_3} D_{\text{Eff,FeCl}_2} M_{\text{Fe}} p_{\text{i,FeCl}_2}}{R_{\text{FeCl}_2} T l_{\text{Ox}}} 
\]

Equation 11

Following integration an equation for the evolution of the oxide layer depth, \( l_{\text{Ox}} \), is obtained, as shown in Equation 12:

\[
l_{\text{Ox}} = \sqrt{\frac{1}{\rho_{\text{Fe}_2\text{O}_3} M_{\text{FeCl}_2}} \frac{M_{\text{Fe}_2\text{O}_3} D_{\text{Eff,FeCl}_2} p_{\text{i,FeCl}_2}}{R_{\text{FeCl}_2} T} t}
\]

Equation 12

where \( t \) is time in seconds.

The methods of dealing with \( D_{\text{Eff,FeCl}_2} \) is the distinction between the LFM and PCM models. The Labyrinth Factor Method (LFM), which has been used in previous work\(^{10,19,24}\), does not explicitly calculate \( D_{\text{Eff,FeCl}_2} \). Instead, it fits a curve to experimental data, and is optimised here using least squares. With sufficient data points, the LFM can be used to extrapolate corrosion depth for well-characterised experimental conditions. In order to have reliable predictive capability for a given set of experimental conditions, 7-28 days of test data are typically required. The PCM uses simplified but physically-based modelling to predict \( D_{\text{Eff,FeCl}_2} \) evolution over time. Determining the duration of test data required for the PCM is one of the objectives of this work. The LFM and PCM methods are described in detail in the next sections. Both models assume that the corrosion depth increases uniformly based on the experimental observations.

Table II List of variables and constants used in equations

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<th>Units</th>
<th>( M_{\text{Fe}_2\text{O}_3} )</th>
<th>( M_{\text{FeCl}_2} )</th>
<th>( p_{\text{i,FeCl}_2} )</th>
<th>( \rho_{\text{Fe}_2\text{O}_3} )</th>
<th>( R )</th>
<th>( T )</th>
<th>( M_1 )</th>
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<td>159.69</td>
<td>126.751</td>
<td>20.2</td>
<td>5240</td>
<td>8.314</td>
<td>813</td>
<td>873</td>
<td>126.751</td>
<td>14.0067</td>
<td>1</td>
<td>3.64</td>
</tr>
</tbody>
</table>
Labyrinth Factor Method (LFM)

In this method $D_{\text{Eff}, \text{FeCl}_2}$ is calculated by combining the molecular diffusivity of a diffusing gas through a quiescent background gas ($D_{M, \text{FeCl}_2}$) with a labyrinth factor ($\lambda$) as shown in Equation 13. The labyrinth factor accounts for the porosity and tortuosity of the oxide layer and is determined using experimental data$^{10,24}$.

$$D_{\text{Eff}, \text{FeCl}_2} = \lambda D_{M, \text{FeCl}_2} \quad \text{Equation 13}$$

The molecular diffusivity, $D_{M, \text{FeCl}_2}$ is calculated using the Chapman-Enskog equation$^{24,29}$ shown in Equation 14 and assuming suitable values for the collision diameter, $\sigma^{12}$ of FeCl$_2$ molecules.

$$D_{M, \text{FeCl}_2} = 1.86 \times 10^{-7} T^{rac{3}{2}} \frac{\left( \frac{1}{M_1} + \frac{1}{M_2} \right)^{rac{1}{2}}}{p \sigma^{12}_{12} \Omega} \quad \text{Equation 14}$$

where $D_{M, \text{FeCl}_2}$ is the diffusivity in m$^2$/sec, $M_1$ and $M_2$ are the molecular weights of the diffusing and background gases, respectively, $p$ is pressure, $\sigma^{12}$ is the collision diameter of the diffusing and background gases and $\Omega$ is the temperature dependent collision integral. $M_1$ corresponds to FeCl$_2$ here and the molecular weight of the background gas $M_2$ is that of pure nitrogen, since flue gas consists of $\approx$ 70\% by volume nitrogen.

Predictions from the Chapman-Enskog kinetic theory are limited due to the requirement for estimates of the collision diameters and collision integrals; such estimates are not available for all gases$^{29}$. $\sigma^{12}$ is the arithmetic average of the values for the two species present, which are tabulated for certain gases in work by Cussler$^{29}$. Values of the dimensionless quantity $\Omega$ are generally of the order 1 and its calculation depends on an integration of the interaction between two species, which is described by the Lennard-Jones 12-6 potential$^{29}$. Values for iron chloride gas are not yet available, so values are assumed in a manner similar to Stott and Shih$^{24}$ and given in Table II.
The labyrinth factor is determined following the analysis of experimental results and optimised using a least squares objective function for a power law as shown in Equation 15 where \( l = a\sqrt{t} \) in order to accurately describe the square root function as shown in Equation 12.

\[
a = \exp\left(\sum_{i=1}^{n}\ln l_i - 0.5\sum_{i=1}^{n}\ln t_i \right) / n
\]

Equation 15

where \( n \) is the number of sample experimental points to be used for the least squares fit.

From combining \( l = a\sqrt{t} \), Equation 12 and Equation 13 for \( D_{Eff,FeCl2} \) we get an equation for the labyrinth factor \( \lambda \) as shown in Equation 16:

\[
\lambda = a^2 \frac{M_{FeCl2} \rho_{FeO} R_{FeCl2} T}{D_{M,FeCl2} M_{FeCl2} \rho_{FeCl2}}
\]

Equation 16

Provided there is sufficient experimental data available, the LFM, using least-squares can be used to make predictions for longer exposure times.

**Porosity-based Corrosion Method (PCM)**

The porosity-based corrosion method (PCM) adopts a physics-based approach to determine values for \( D_{Eff,A} \), as follows\(^{30,31} \):

\[
D_{Eff,FeCl2} = \varepsilon^2 \left( \frac{1}{D_{M,FeCl2}} + \frac{1}{D_{K,FeCl2}} \right)^{-1}
\]

Equation 17

In this method \( D_{Eff,FeCl2} \) is calculated by combining molecular diffusivity \( D_{M,FeCl2} \) with Knudsen diffusivity \( D_{K,FeCl2} \) and the porosity of the oxide layer, \( \varepsilon \), found from testing. This model contains contributions from both bulk (molecular) and pore (Knudsen) diffusion to the rate of mass transport through the oxide layer. This allows for the possibility of bulk diffusion becoming dominant over pore diffusion in the model. This would occur as the porosity term tends towards 1 and the \( D_{K,FeCl2} \) value...
tends towards ∞ (as \( \bar{r} \) increases in size), due to cracks forming in the oxide. Knudsen diffusivity is calculated as:

\[
D_{K, FeCl_2} = 97\bar{r}\left(\frac{T}{M_1}\right)^{0.5}
\]  

Equation 18

where \( \bar{r} \) is the average pore radius in m and \( D_{K, FeCl_2} \) is the Knudsen diffusivity in units of m\(^2\)/s. \( D_{Eff, FeCl_2} \) is then calculated as shown in Equation 17\(^30\).

Equation 12 gives the oxide layer depth predictions. It is proposed here to determine the value of \( \varepsilon \) from experimental results. As previously stated, the exact duration required for these experiments is examined in this work. Future development of the PCM will involve prediction of \( \varepsilon \) so that the need for experimental characterisation will be further reduced. SEM images are obtained from the samples which have been exposed to the synthetic salt. From these samples an oxide layer is identified. The image is processed as seen in Figure 9 (a) using OLYMPUS Stream Motion\(^{32}\) image analysis software to obtain the total area of the oxide layer on the sample (\( A_{Total} \)).

![Figure 9 Images of a representative porous oxide layer, showing the area used to calculate porosity values (a) SEM image (b) binary version of image](image)

The image is converted to binary via a colour contrast analysis, as in Figure 9 (b). The pores in the
oxide layer can thus be clearly identified and analysed. The area of each individual black and white section in the image is thus quantified and the cumulative area of the pores in the sample ($A_{pores}$) is obtained. The porosity of the oxide layer is the ratio of the area of the pores to the total area of the oxide, i.e.

$$\varepsilon = \frac{A_{pores}}{A_{total}}$$  \hspace{1cm} \text{Equation 19}

The Olympus Stream software also provides measurements for the mean radius of the pores detected in the oxide layer. The software obtains measurements for pore radii via the following technique:

1) The centre of gravity of each pore is determined.
2) Lines are plotted through the centre of gravity at $1^\circ$ circumferential increments and intercept points with the outer edge of the pore are determined.
3) A local diameter of the pore outer edge is then determined for each circumferential increment. The diameter is defined as the distance between the two intercept points with the outer edges.
4) From this a maximum, minimum and a mean diameter is calculated for that pore.

From these measurements the average pore radius $\bar{r}$ of each pore is obtained and used to determine an overall average pore radius for the sample.

**Results and Discussion**

**Experimental**

This section presents results from the experiments carried out on samples exposed to the synthetic salt at 540 °C for times of 1, 4, 7, 14, 21 and 28 days. SEM results and optical microscopy results are analysed and the mechanism observed is discussed. Similar tests were also performed at 600 °C, but for reasons of space, are not presented here in detail. Please refer to the supplementary material for images.
of SEM and EDX element mapping.

Figure 10 shows SEM images of the specimen cross section area (see Figure 6) for exposure times of 1 to 28 days. After 1 day, a cupola (dome of oxide) has formed over a section of the iron (Figure 10 (a)). This cupola is formed by evaporating iron chloride and its shape corresponds to that of the stagnant diffusion boundary layer of FeCl$_2$ entering the bulk gas phase above the sample as described by Zahs et al.$^{18}$ A porous oxide layer has also begun to form on the surface of the sample substrate.

The sample exposed for 4 days shows a cupola, which has completely detached from the substrate and porous oxide layer (Figure 10 (b)). A uniform oxide layer has now formed over the substrate and is separated from the substrate. Following 7 days exposure a large void space has appeared below the cupola (Figure 10 (c)) and there is evidence of portions of oxide below the cupola, although they appear to have further deteriorated. This breakdown of the protective oxide scale is similar to that discussed by Jonsson et al.$^{17}$, which describes an accelerated attack that occurs following breakdown of the initial protective oxide layer.
Figure 10 SEM images of iron after exposure to synthetic salt at 540 °C for (a) 1 day; (b) 4 days; (c) 7 days; (d) 14 days; (e) 21 days; (f) 28 days
Examination of the sample exposed for 14 days in Figure 10 (d) appears to show uncorroded iron separated from the substrate. This is also seen following examination of the sample following 21 days exposure. A section of uncorroded iron can be seen detaching from the substrate in Figure 10 (e). This undermining of uncorroded iron is of interest and the mechanism behind this process requires further investigation.

Figure 10 (f) shows a sample exposed for 28 days. A uniform compact oxide layer has formed over the substrate. This oxide is detached from the substrate and does not provide protection against further attack. Portions of oxide have also mixed with the salt particles. Enestam et al.\(^{15}\) have defined the uniform compact oxide layer as Type 1 oxide and the porous oxide which is “sprawled around and between salt particles” as Type 2 oxide.

Figure 11 (a) shows an image of the sample exposed for 28 days at a higher magnification than Figure 10 (f). The Type 2 oxide can be seen amongst the salt layer. The uniform Type 1 oxide layer can also be seen as well as the void space between the Type 1 oxide and the substrate.

The formation of Type 2 oxide may have occurred following the deterioration of the previous thinner cupolas and porous oxide layers to such an extent that they fragment and mix with the salt layer in a manner similar to spalling. Spalling occurs in corrosion when the substrate sheds particles of corrosion product. The postulation of Type 2 oxide forming from severe deterioration of Type 1 oxide is supported by the fact that these thinner cupolas and oxide layers, which are visible in samples exposed for shorter time periods, can no longer be seen in the longer term tests.

Figure 11 (b) shows a further magnified view of the same 28 day sample shown in Figure 11(a). This image reveals the porosity of Type 1 oxide at this stage. A thin broken oxide layer can also be seen above the Type 1 oxide. This is not visible at lower magnification and may be a residue of a previous Type 1 oxide layer. This layer has almost fully broken up and mixed with the salt layer, forming Type 2 oxide.
An optical microscope image is shown for the sample exposed for 21 days in Figure 12 under dark light. This image shows uncorroded iron on the top portion, which has separated from the substrate. The bottom portion, closer to the substrate, has been oxidised. This indicates a two-stage mechanism whereby uncorroded iron is undermined by a thin oxide layer before subsequently oxidising. As the iron is subjected to oxidation from two sides, the corrosion rate is expected to increase.

As will be illustrated later in Figure 13, the chemical composition of the substrate consists of pure iron. The oxide layers consist of both iron and oxygen, uncorroded iron has been shown to consist of
pure iron with oxygen present along the edges of the portions which have separated from the substrate.

EDX elemental maps of the cross sectional areas have been obtained to determine the chemical composition of a section of the samples. Maps are presented for samples which were exposed for 14 and 28 days. Figure 13 shows the 14 day sample analysed and the corresponding element maps of Fe, O, Ca and S; from this image a uniform, compact, porous oxide layer is visible. A portion of uncorroded iron which has almost fully separated from the substrate is also visible.

The concentration of iron in the porous oxide layer is less than that of the uncorroded iron which has detached from the substrate. The separation between the different layers can be seen in the image. There is no evidence of Type 2 oxide in this image. A layer of oxygen is visible on top of the substrate and on the porous oxide layer with no oxygen present in the uncorroded metal, which has separated from the substrate. Calcium and sulphur are also shown to be present in the salt layer, as expected (see Table I).

The uncorroded metal, which has detached from the substrate, contains no oxygen except at its edges, confirming that it is not yet fully part of the oxide layer, but is being oxidised from two sides. A layer of oxygen also exists on top of the substrate indicating that the oxidation process has begun at this location.

It is noted that other elements are present however they do not produce informative maps for a number of reasons. These include low concentrations of the elements, resulting in background elements becoming dominant. Also in the case of Cl₂, the high volatility of FeCl₂ in the vacuum of the SEM chamber may result in its evaporation.
Figure 13 SEM image and EDX element maps of the sample following exposure to synthetic salt for 14 days at 540 °C.

The 28 day sample analysed using EDX and corresponding elemental maps of Fe, O, Ca and S are shown in Figure 14. Both Type 1 and Type 2 oxide are present in this image. A clear void space also
exists in this image showing the separation of the oxides from the substrate. Type 1 oxide can be seen in the form of a compact uniform layer over the substrate. Type 2 oxide debris can also be seen mixed with the salt layer in the epoxy.

A layer of oxygen is visible at the top of the substrate and along the entire Type 1 oxide layer. There does not appear to be any uncorroded metal separated from the substrate. Uncorroded metal which had separated may have been fully oxidised following the 28 days exposure. Again the presence of calcium and sulphur in the salt can be seen.

Comparison of the 14 and 28 day results shows the evolution of the corrosion process. After 14 days no Type 2 oxide is present, a porous Type 1 oxide layer is present with a layer of uncorroded iron detached from the substrate beneath it. This uncorroded iron has begun to oxidise from two sides. After 28 days Type 2 oxide is present and there appears to be no uncorroded iron separated from the substrate; there is however a thick porous oxide Type 1 oxide layer.

Based on observations, the corrosion process is proposed to proceed via the following stages:

1) Initial corrosion of fresh substrate, forming a closely adherent Type 1 oxide layer on substrate surface with a cupola forming over this.

2) Detachment of the oxide layer from the substrate.

3) Fragmentation of the detached layers of oxide leading to formation of Type 2 oxide.

4) Undermining of uncorroded iron, which detaches from substrate

5) Oxidation of detached iron from two sides leading to formation of a new uniform type 1 oxide layer with oxide also forming on substrate surface

6) Detachment of this new oxide formed on substrate surface and fragmentation of the detached layers of oxide leading to formation of Type 2 oxide.
Figure 14 SEM image and EDX element maps of the sample following exposure to synthetic salt for 28 days at 540 °C

The iron corroded with no salt coverage was also analysed using optical microscopy. After 1 day an initial thin, 11 µm uniform oxide layer has formed on the substrate surface. The sample exposed for 4 days displays a thicker oxide layer which is still in contact with the substrate. This is different to the
sample with salt, where the oxide layer is detached from the substrate after 4 days. Following 7 days exposure, the porous oxide layer which has grown in thickness to approximately 28 μm has begun to detach from the substrate with voids visible between the substrate and oxide. However compared to the sample with salt, which has a thickness of approximately 84 μm (after 7 days), the severity of corrosion is significantly less and the oxide is more integrated with the substrate, and therefore more protective.

The 14 day, no-salt sample showed clear detachment of the oxide layer from the substrate. After 21 days, this oxide layer has split into two separate layers which are no longer considered protective. After 28 days, the oxide layer has fragmented significantly and fresh substrate is again exposed to the atmosphere.

The evolution of corrosion depths was measured using the method previously described with between 15 and 20 sample measurements taken across the specimen width. Measurements of corrosion depths are shown in Figure 15 for samples with and without the synthetic salt. Of specific interest here is the effect of salt-induced corrosion compared to without salt. Information of the corrosion depth is critical for calibration of the LFM and for validation of both models.
It was difficult to obtain accurate measurements for samples exposed to the salt for long duration tests due to oxide fragmentation and mixture with the salt. The apparent decrease in corrosion depth seen in Figure 15 after 28 days is attributed to this fragmentation process. The SEM provides more detailed information regarding the corrosion layer structure, due to its superior image quality. Pores can be identified from these images if examined at a high enough magnification and therefore these images were used to obtain the porosity data for use in the PCM.

The detrimental effect of the salt on the corrosion rate is clear from Figure 15. The samples without salt applied are subject to pure oxidation and display a significantly lower corrosion rate than the samples with synthetic salt at the same conditions. This highlights the accelerated corrosion process due to alkali halide containing deposits and the need to develop a greater understanding of it.

Figure 15 Thickness of the corrosion depth under optical and SEM with and without salt applied at 540 °C. Uncertainty bars represent a ± standard deviation.
Modelling – Labyrinth Factor Method (LFM)

The corrosion depths from the optical microscopy have been used in the least squares fit identification process to obtain the labyrinth factor $\lambda$ and the corrosion coefficient $a$ for the LFM model; as tabulated in Table III. In order to evaluate the extrapolation capability of the LFM, values for $a$ and $\lambda$ have been obtained for $n=1$ (1 day), $n=2$ (1, 4 days), $n=3$ (1 to 7 days), $n=4$ (1 to 14 days), $n=5$ (1 to 21 days) and $n=6$ (1 to 28 days). As can be seen from Table III the values begin to converge after $n=3$ (1 to 7 days), with the difference being negligible for cases using data after days 21 to 28.

Table III Calibrated values of $a$ and $\lambda$ using least squares fit to experimental data.

<table>
<thead>
<tr>
<th>$n$</th>
<th>1 (1 Day)</th>
<th>2 (1 to 4 Days)</th>
<th>3 (1 to 7 Days)</th>
<th>4 (1 to 14 Days)</th>
<th>5 (1 to 21 Days)</th>
<th>6 (1 to 28 Days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>$2.311 \times 10^{-6}$</td>
<td>$2.689 \times 10^{-6}$</td>
<td>$3.507 \times 10^{-6}$</td>
<td>$3.653 \times 10^{-6}$</td>
<td>$3.837 \times 10^{-6}$</td>
<td>$3.829 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>$1.98 \times 10^{-4}$</td>
<td>$2.68 \times 10^{-4}$</td>
<td>$4.56 \times 10^{-4}$</td>
<td>$4.95 \times 10^{-4}$</td>
<td>$5.46 \times 10^{-4}$</td>
<td>$5.43 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Note: For each case all data points up to and including exposure time for that case are included in the least squares fit

Figure 16 shows the predicted LFM corrosion depth measurements for the values of $a$ and $\lambda$ identified in Table III, along with the measured experimental data. It is clear that there is sensitivity to the number of days of test data used ($n$). There appears however to be convergence for $n \geq 5$ (1-21 and 1-28 days), indicating the duration of test data required to calibrate the LFM. Previous work has suggested that data from up to 7 days testing is appropriate for reproducible, relevant information regarding the corrosion tendency of steels\textsuperscript{26} and the results of Figure 16 corroborate this to some extent. It is noted that for models such as the LFM, which use measurements of samples that may contain Type 2 oxide, which is difficult to measure at longer exposure times, an underestimation of the corrosion rate is possible.
Modelling – Porosity Based Corrosion Model (PCM)

Values of porosity ε and average pore radius \( \bar{r} \) of the oxide layer for use in the PCM method have been identified for 6 different exposure times, 1 day only, 4 days only, 7 days only etc. as shown in Table IV. These results provide an insight into the evolution of the oxide layer, as shown in Figure 17. The porosity level is seen to remain relatively constant with respect to exposure time. In contrast, the average pore radius in the sample increases at an almost linear rate. Future development of the PCM will incorporate a theoretical approach for the void/pore growth to obtain values of \( \varepsilon \) and \( \bar{r} \). This will further reduce the need for experimental characterisation.

Figure 16 Results obtained for LFM method using experimental (optical microscopy) data from 1, 4, 7, 14, 21 & 28 days at 540 °C and the least squares method
Table IV Measured values of porosity $\varepsilon$ and average pore radius $\bar{r}$ for different exposure times at 540 °C.

<table>
<thead>
<tr>
<th></th>
<th>1 Day</th>
<th>4 Days</th>
<th>7 Days</th>
<th>14 Days</th>
<th>21 Days</th>
<th>28 Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$</td>
<td>0.052</td>
<td>0.046</td>
<td>0.060</td>
<td>0.054</td>
<td>0.060</td>
<td>0.058</td>
</tr>
<tr>
<td>$\bar{r}$ (μm)</td>
<td>0.341</td>
<td>0.542</td>
<td>0.992</td>
<td>1.124</td>
<td>1.626</td>
<td>2.143</td>
</tr>
</tbody>
</table>

Figure 17 shows the change in porosity and pore radius when examined for the test samples exposed for increasing time periods. As has been found the porosity remains relatively constant with the pore radius increasing at an almost linear rate. Using this experimental data and the least squares technique, an equation for pore growth over time can be obtained. In order to further investigate the growth of pore radius with respect to the exposure time, a histogram showing the percentage occurrence of a range of pore radii in the oxide is shown in Figure 18.
The vast majority, approximately 95% of pores, following 1 day of exposure, are less than 1 μm in radius, with the remaining 5% being in the range of 1 to 2.0 μm. The longer term tests show a continuous trend towards a greater average pore radius. Less than 10% of pores in the sample exposed for 28 days are found to be less than 1 μm in radius with approximately 25% being between 2 to 3 μm and 12% being greater than 4 μm in radius. It appears that as smaller pores grow they coalesce to form larger pores. The porosity remains relatively constant despite this coalescence due to the increasing thickness of the layer, resulting in a larger overall oxide area.

For the initial results obtained from the PCM, average values have been taken for both $\varepsilon$ and $\bar{r}$ from all values obtained for shorter exposure term tests. The 1 to 7 day sample values for $\varepsilon$ and $\bar{r}$ use the average value of the 3 data points obtained from the 1, 4 and 7 day samples. The results are shown in Figure 19. Figure 19 shows that the day on which $\bar{r}$ is selected impacts predicted corrosion depth.
is to be expected because \( r \) increases with time, so later values of \( r \) give greater values of \( D_K, D_{Eff} \) and therefore corrosion depth growth. It is noted that an increase in the size of \( r \) does not result in a linear increase of the corrosion depth. \( D_K \) is linearly dependent on \( r \), however \( D_{Eff} \), which combines \( D_K, D_M \) and \( \varepsilon \), is not.

![Graph showing corrosion depth vs. time](image)

**Figure 19** Results obtained for PCM predictions using average measured porosity data from different exposure times compared to experimental data at 540 °C

As previously stated, the PCM does not yet include a physical submodel for the evolution of \( r \) and \( \varepsilon \).

To observe the effect of an evolving \( r \), Figure 20 provides PCM predictions for \( r \) as a function of time. For these curves, \( n \) indicates the number of data points used to construct the \( r \) function. Due to the highly linear nature of \( r \) evolution, see Figure 17, convergence is seen for \( n \geq 2 \). Figure 20 also compares the performance of the LFM calibrated by \( n=1 \) (1 day) and \( n=6 \) (28 days) test data and the PCM with \( r \) growth modelled on \( n=1-6 \) (1-28 day) test data. In general, the LFM under-predicts the measured trend while the PCM over-predicts it.
As highlighted in Figure 15, long term test samples show significant degradation, making corrosion depth measurement difficult. Since the LFM requires a least-squares fit from experimental results up to 21 and 28 days, inaccurate measurements can result in inaccurate model predictions. It is therefore suspected that the LFM underestimates the true corrosion depth. Over-prediction compared to experimental data is therefore desirable. The PCM predicts convergence for \( n \geq 2 \).

Further tests have been carried out at 600 °C and the results are displayed in Figure 21. Corrosion measurements have been obtained and are compared to both the LFM and PCM methods. It is noted that the corrosion depth does not appear significantly different than that seen at 540 °C as shown in Figure 15. It is possible that not all corrosion is captured using the current measurement methods at 600 °C. The partial pressure of the FeCl₂ gas diffusing outwards at 600 °C is approximately an order of magnitude higher than that at 540 °C as shown in Figure 3. It is possible that as FeCl₂ diffuses outwards
very rapidly, it is not converted to Fe₂O₃ (reaction R4) until it travels further from the substrate and is thus not captured in the oxide layer measured.

Figure 21 Graph comparing results from the LFM, PCM and experimental work at 600 °C

For future studies, initial porosity measurements which have been incorporated into the PCM will be modelled by a theoretical approach for pore growth. This will replace the need for measured data for ε and r. For application to more complex alloys a number of additional aspects will need to be considered. Additional oxides and chlorides such as chromium oxide/chloride and mixed oxides/chlorides will need to be taken into consideration. The oxides will thus be more complex with a number of layers of different oxides expected. Future work will also examine the role of inter-granular penetration of Cl₂ in the overall process³³,³⁴.

Conclusions

The physical process and mechanisms of corrosion of pure iron were studied for different exposure
times from 1 to 28 days at temperatures of 540 °C and 600 °C, both with and without deposition of alkali-halide containing synthetic salt, representative of the ash formed during the biomass co-firing combustion process. Optical microscopy, SEM and EDX has revealed the key stages in the corrosion process. These are: (1) initial corrosion of fresh substrate producing Type 1 oxide, (2) detachment of oxide from substrate, (3) fragmentation of detached layers due to pore coalescence resulting in formation of Type 2 oxide, (4) undermining of uncorroded iron, (5) oxidation of uncorroded iron and fresh substrate, (6) detachment of oxides, continued oxidation and fragmentation.

The key physical role played by the porous oxide layer, vis-à-vis the rate-limiting, outward diffusion of FeCl₂, is thus identified as the basis for a novel corrosion model for the accelerated corrosion due to alkali halide-containing deposits. This model is thus called the porosity based corrosion model (PCM) and is based on observations of porosity and pore radius of the oxide layer, which are used to calculate an effective diffusivity for FeCl₂ gas diffusing through the porous oxide layer. The porosity of the oxide layer remains relatively constant for different exposure terms while the pore radius was found to grow at an almost linear rate. This provides the further opportunity for future development of a model incorporating pore growth, such as the random pore model 35,36. It is postulated that smaller pores coalesce to form larger pores as time passes, leading ultimately to fragmentation of the oxide. Comparison of the PCM to the widely-used LFM indicates that the PCM provides a conservative estimate of corrosion depth. This is not an undesirable outcome as the long-term test data needed to calibrate the LFM can be difficult to obtain due to significant degradation of oxide layers. Future work will focus on the incorporation of a pore-growth model into the PCM and an examination of the role of inter-granular Cl₂ penetration.

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References


32. Anon. OLYMPUS Stream Motion Image analysis software. Germany: Olympus Soft Imaging Solutions GmbH.


